

SIMPLIFYING PROTECTION SYSTEM TO PROLONG CELL LIFE

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Abstract

Cathode materials mainly deteriorate through physical erosion and chemical / electrochemical corrosion. The wear patterns are characterised by a "W-shape" and localised potholes. A variety of materials such as alpha alumina and refractory hard materials have been used for protecting conventional cathodes. TiB₂ based refractory hard materials are well suited for this. They satisfy the electrical conductivity requirements, have a very low solubility in molten aluminium and are wetted by aluminium providing potential benefit in modifying design and operation.

This study was to explore the potential of increasing life for graphitised cathodes using TiB₂ grains without compromising metal purity, cell performance or lining design. Statistical analysis of measurements confirms that cathode life could be increased by at least 2 years. The study revealed that cathode life could be increased by at least 2 years. Increases in B and Ti impurities seen in pot metal were within casthouse tolerance limits.

Introduction

Smelters are pushing for higher productivity and thus increased current densities and this is associated with a decrease in the life of cells as shown in Figure 1 [1].

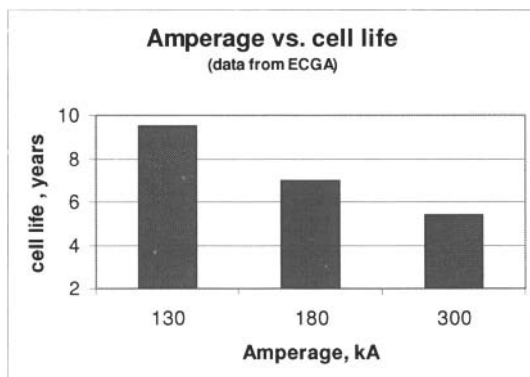


Figure 1: Amperage vs. cell life – data from [1]

At the same time due to demands for higher thermal and electrically conducting cathodes these are being made with higher graphite content with less resistance to mechanical

erosion[2]. Hence the effort to increase cathode or cell life is relevant. The end result of increasing production of aluminium and lower cell life is more spent potlining waste and a figure of 13.2 kg/t Al is suggested [3]. The low solubility of TiB₂ in aluminium makes it a suitable material to protect the cathode [4]. See also Figure 2 .

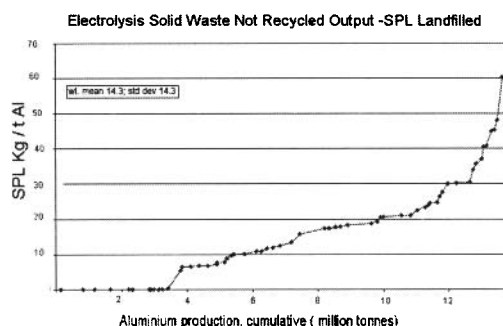


Figure 2: SPL generation statistics [3]

Deterioration mechanisms for cathode are well known [5,6,7]. The cathode wear in modern electrolytic cells is typically of "W" shape pattern, with troughs near the sidewall [8] due to higher electrochemical wear in zones of increased current density (Figure 3).

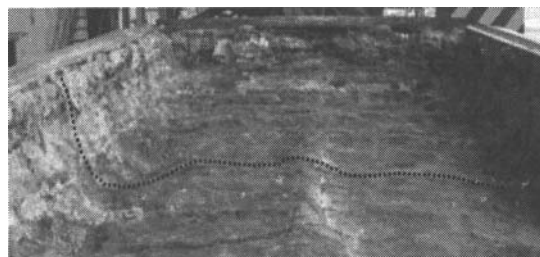


Figure 3: "W" shaped erosion [3]

One of the primary routes for cell failure is through the cathode bottom [5,9]. Use of TiB₂ to protect the cathode and thus improve cathode life is by no means a new idea and coatings of TiB₂ have been tried in the past [10,11,12]. However, in this paper, we are reporting on a new approach: the addition of granular TiB₂ to operating electrolysis cells. This approach was chosen as it was simple and expected to be effective provided a layer of sufficient thickness could be maintained. The impact of the

addition of the TiB₂ on metal quality will be dealt in part II of this paper [13].

Trial design and implementation

Two adjoining cells of the same age and design with graphitised cathodes operated at similar operating parameters were selected as test and control cells for the trial. The addition was limited to only one test cell due to high cost of TiB₂ and to minimise potential risk to downstream product quality. The quantity of TiB₂ to be added was estimated at 290 kg based on solubility product (K_{sp}) of TiB₂. An initial TiB₂ layer of about 18 mm on the cathode was expected assuming uniform distribution and no compaction. A minimum thickness of 4 mm would be expected if the material compacted to the true density.

14 kg of the TiB₂ grains were added during each anode change thus taking one full anode cycle of about 26 days to complete the addition. The analysis of TiB₂ grains is shown in Table 1 and Table 2. Samples A and B represent two batches and a 50/50 mixture of these was used.

Table 1: Chemical analysis of TiB₂

Element, Weight %	Sample A	Sample B
Boron	30.6	31.2
Titanium	67.6	67.2
Iron	0.11	0.19
Oxygen	1.58	0.73
Carbon	0.26	0.41
Phosphorous	< 1 ppm	-

Table 2: Physical properties of TiB₂

Parameter	Sample A	Sample B
Bulk Density (tapped), g/cm ³	1.05	1.05
Real Density, g/cm ³	4.51	4.51
Particle Size, %		
+ 4.76 mm	22.1	56.2 (-6.3+4mm)
+ 2.36 mm	48.4	
+ 1.18 mm	69.6	
- 1.18 mm	30.4	
+ 45 μm	----	
- 45 μm	----	

Four sets of cathode erosion measurements were performed on the operating test and control cells before and during the trial over a period of about two years. In addition, two sets of measurements were done in two other cells of same design and age in order to ensure that sufficient base data was available in the early stages. After about 2 years the test cell was cut out and a partial autopsy done to inspect condition of cell as well any residual TiB₂. Detailed erosion measurements were done in the cut out cell Both anode and cathode centre line referencing

methods were used to allow comparison with earlier measurements in operating test cells and with cut out cells of similar design which are normally measured using the cathode centreline as reference.

Erosion measurement in operating test and control cell

The procedure assumes no cathode heave is taking place. The measurements were performed during routine anode changes and a complete set of measurements took about 26 days. By studying the erosion rates in the maximum erosion zone, the cathode life for the test and control cells could be predicted. Measurements were made using a special tool, based on earlier design [14], that was developed to suit the cell design used in the plant (Figure 4).

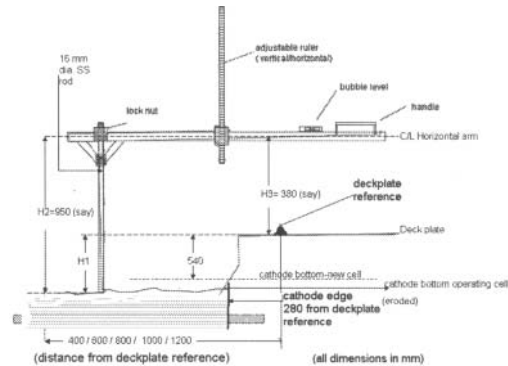


Figure 4: Cathode erosion measurement tool

Fifteen measurements were performed per anode location with a total of 300 data points for all 20 anodes as shown in Figure 5.

For illustrating, the locations are shown for anodes 1 and 2 in Figure 6 these being near the tap end and the corresponding cathode numbers were 19 to 16. For anode 1 and anode 20 opposite to each other, there would hence be three columns of data with each column having 10 data points, 5 of them from anode 1 and five from anode 20. For reporting, the columns were numbered from 1 to 30 starting from anode 1(right). It is seen from Figure 6 that there may be measurements quite far away from the centreline of the cathode block, where normally maximum erosion is observed in industrial cells. Fortunately there were 10 columns of data (100 data points) that were within 50 mm of the centre line of cathode and hence this concern could be addressed.

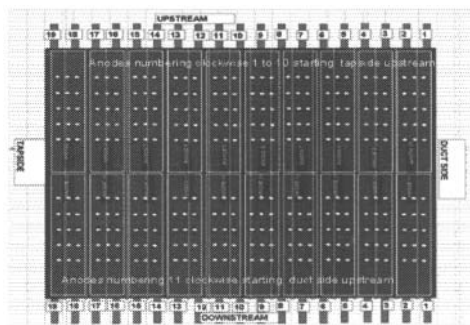


Figure 5: Anode shadow on cathode surface

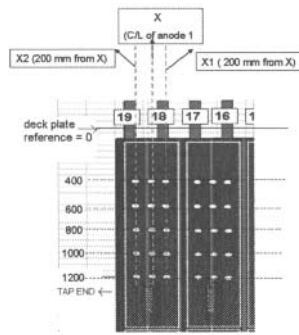


Figure 6: Measurement positions (figures in mm)

The surface contours for the first and fourth set of measurements in the operating test cell for the entire set of 300 data points are shown in Figure 7 and Figure 8.

Similar data for 300 data points from the operating control cell are shown in Figure 9 and Figure 10. These graphs are with same orientation as in the figure showing measurement positions, namely that tap end of the cell is to the left and upstream locations are at the top. These surface contours reveal clearly that the cathode is eroding over time for both the test cell and control cell but the control cell erosion is much more than for the test cell during the same time interval.

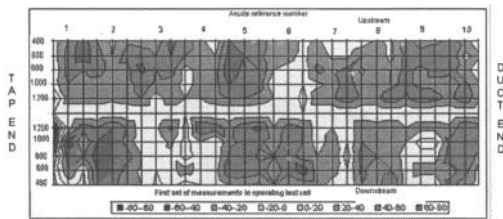


Figure 7: Erosion contour – test cell 1st set

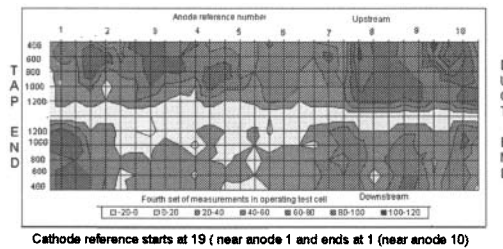


Figure 8: Erosion contour – test cell 4th set

Erosion is seen to be higher in the same zones namely near anodes 7 to 10 corresponding to cathodes 2-7. Thus it is seen that the procedure developed was adequate even though the accuracy of individual measurements was probably ± 1 cm. Typically there is maximum erosion at centre line of each cathode block but since there were 300 points measured in the cell, there were more than 30% of the data points that were close to the cathode centrelines and hence the anode referencing method adopted though not ideal was adequate.

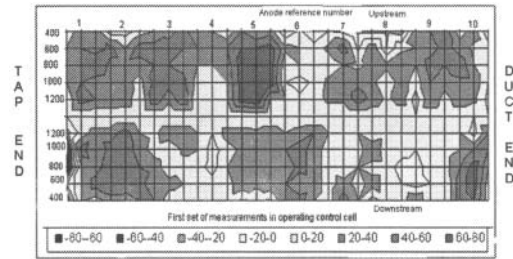


Figure 9: Erosion contour – control cell 1st set

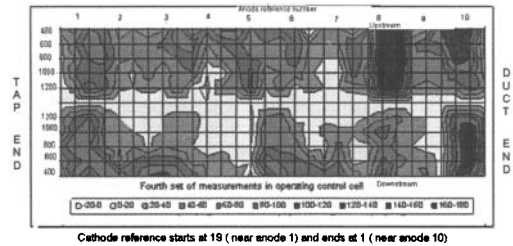


Figure 10: Erosion contour – control cell- 4th set

Erosion rates estimated from the measurements and presented in Figure 11 show that the addition of TiB_2 has resulted in significant reduction in the rate. The life for test cell was estimated using a more conservative wear rate of 26 mm/year to be 3.6 years more than the control cell. Based on the expected life of the cell using this rate and the consumption of TiB_2 estimated from solubility product and other factors, it was estimated that adding 450 kg of TiB_2 would result in optimum level of protection. If one were to add this at the beginning of cell operation and assume 26 mm/year erosion, an increase of 5 years can be predicted for cathode life.

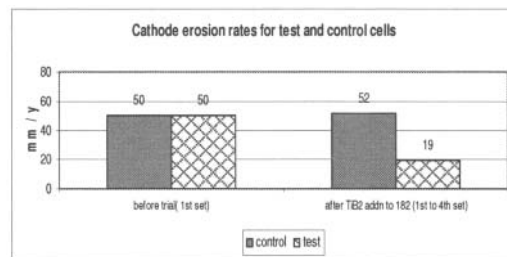


Figure 11: Erosion rates - before & after TiB_2 addition

Since there were four measurements, the rate of erosion can be calculated for different time intervals and to demonstrate that the rate was always slower for the test cell, the estimates are described in Figure 12.

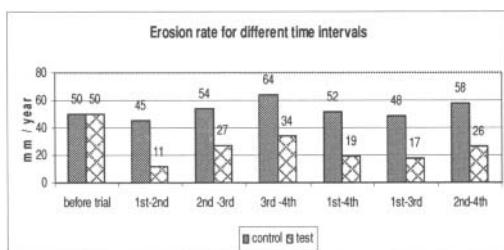


Figure 12: Erosion rates – for different time intervals

Part 2 - Cell autopsy

A set of measurements was done just prior to cut out and repeated in the cut out cell for validation. The average and maxima were reasonably close to each other. Based on the comparison it was concluded that operating cell measurements can give an idea of the erosion patterns and rates but localised measurements can occasionally be off by about 10 -20 mm/year through special events such as positioning errors or freeze. This has been over come to some extent by multiple measurements during the trial. It can also miss steep points of erosion which may be covered by freeze and in addition areas such as centre channel are not possible to measure in operating cells. The practice of using the centre line of the anode and 400 mm of either side of the same for measurements can lead to these being done at times very close to the seam. However, the erosion data from operating cell measurements was found to be good enough to draw conclusions, namely that TiB₂ addition is improving the cathode life substantially and to provide an estimate of the rate of erosion and cathode life.

Erosion measured by standard procedure

Standard erosion measurements were carried out at 57 points after cut out at the centre line of the cathode for test cell and another cell of similar design. The maximum erosion zone was in the upstream area and the rate of erosion was lower for test cell by 11 mm/year at the maximum erosion point. The cathode life for the test cell was estimated to be more than 1.79 years longer than the control cell but this increase would have been greater if TiB₂ was added from start of operations.

The average erosion rate value for the upstream locations was significantly lower by 20 mm for test cell as compared to cell G by Student's t-test of significance at 99% confidence interval.

Residual TiB₂

Inspection and analysis showed TiB₂ grains to be present in cut out test cell after 2 years of operation. The TiB₂ added did not seem to be bound to the cathode carbon or to enhance the wetting of the cathode surface although the particles were wetted by metal. The grains appeared to be mobile and not uniformly distributed on the surface of cathode. From analysis of this agglomerated grains wetted by metal it was concluded that the material is a mixture of

TiB₂ with metal. The grains seemed to be mobile and not bound to the cathode carbon. TiB₂ particles added originally were coarse aggregates of more than 1 mm and tended to break up easily. From this it was concluded that nature of TiB₂ has not changed much. A macro view of the cell showing locations of the grains is depicted in Figure 13.



Figure 13: View of test cell after cut out

The grains are covering all areas of the cell except the dark areas visible on the photograph. Two of the areas where grains are visible are shown by arrows but the grains are present in most parts of the cell. The clear evidence of residual TiB₂ in the cell as seen in autopsy was encouraging.



Figure 14: TiB₂ as received

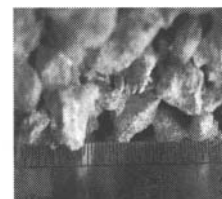


Figure 15: TiB₂ in test cell

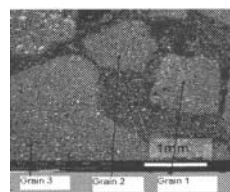


Figure 16: TiB₂ Grains 1 to 3

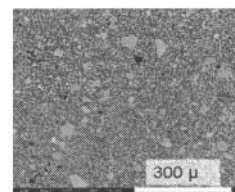


Figure 17: Grain 1- zoomed

Theoretical estimate of TiB₂ consumption

Based on solubility product (K_{sp}) of 10000 ppm³ units (1.825 x 10⁻¹⁸ gram moles³/g³ Al), it is estimated that the initial amount needed to saturate the metal in test cell would be about 0.5 kg. The loss of dissolved TiB₂ due to dilution by produced metal and tapping was estimated to be 0.91 kg/day. Based on these estimates the 290 kg of added TiB₂ was expected to last 3180 days. This did not

take in to account any losses during tapping of bath / metal due entrainment of grains.

Patterns of erosion

By plotting the average and maximum values measured as a function of distance from the reference clearly shows more erosion upstream and downstream close to the sidewall. The wear generally increased from the central channel towards the sidewalls on each side of the cathode block. Upstream erosion is much greater than downstream (Figure 18).

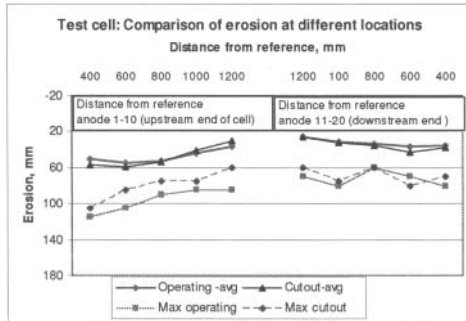


Figure 18: Erosion at different locations

Cell performance and process parameters

Cell performance data was collected for test and control cells and comparison of data showed several features. However there were no adverse effects found. The test cell had more net bath tapped than the control cell and higher AlF_3 consumption for test cell as compared to most of the adjacent cells with similar age indicating that TiB_2 may be protecting cathode from sodium penetration. Freeze profile data and other process parameters such as metal velocity, anode current distribution, superheat and shell temperature were also compared for control and test cell and no major differences seen.

Conclusions

The following can be concluded based on trials

1. Autopsy observations and operating cell measurements confirmed that TiB_2 addition in test cell has reduced erosion rate compared to the control cell without such addition. The expected increase in cathode life can be at least two to three years and can be as high as 5 years if the quantity of TiB_2 was optimised at 450 kg and added at the start of cell operations.
2. The reduction in erosion has not altered the pattern of erosion, namely higher rates of erosion at ends of cathode especially in upstream zone; though even at these locations the wear rate is estimated to be less for the test cell as compared to the control cell. The trends and patterns by measurements both in cut out cell operating cell are similar but measurement in the operating cell understates the erosion.

3. The erosion measurement technique employed in operating cells was acceptable but would benefit from further refinements to align with the central portion of the cathode.
4. A substantial portion of the TiB_2 added to test cell was still present even after 2 years of operation though a mass balance could not be performed.
5. The TiB_2 grains were not uniformly distributed on the cathode surface and were seen to be clearly wetted by aluminium. Zones of high erosion did not have higher amounts of TiB_2 as originally expected prior to the trial. TiB_2 grains with a more optimum particle size distribution that would pack better would be desirable in any future studies so as to minimise movement of the grains.

A lesson from these observations is that would be advisable to use TiB_2 with a better particle size distribution that will pack well so that the grains will be less mobile. It may be also worthwhile to add the TiB_2 as a slurry pre-wetted with aluminium which could minimise movement of grains.

Initial techno economic calculations were done to evaluate the feasibility of this project. These will be confirmed once the population of the test cells is increased for validating the initial results.

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References

1. From ECGA website (carbonandgraphite.org) aluminium_production.pdf as on 7-3-10.
2. J.M. Dreyfus and S. Lacroix, "6.07 - Improvement of Erosion Resistance of Graphitised Cathodes", Eighth Australasian Aluminium Smelting Technology Conference And Workshops, Yeppoon, Australia 3 - 8 October 2004, 9 pages.
3. "Life Cycle Assessment Of Aluminium: Inventory Data For The Primary Aluminium Industry- Year 2005 Update LCS update 2005 - September 2007", from International Aluminium Institute as on 6-3-2010. <http://www.world-aluminium.org/?pg=/Downloads/Publications/Full%20Publication&path=269>
4. N.J. Finch, "The Mutual Solubilities Of Titanium And Boron In Pure Aluminum", Met. Trans. B, 3(10), 1972, 2709-2711.
5. M. Sørli and H. A. Øye, "Cathodes in Aluminium Electrolysis", Aluminium-Verlag, Düsseldorf, 1994.

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6. P. Brisson, G. Soucy, M. Fafard, H. Darmstadt, and G. Servant, "Revisiting Sodium And Bath Penetration In The Carbon Lining Of Aluminum Electrolysis Cell", *Light Metals* 2005, 727-732.
 7. P. Rafiei, F. Hiltmann, M. Hyland, B. James, and B. Welch, "Electrolytic Degradation Within Cathode Materials", *Light Metals* 2001, 747-752.
 8. A. Schnittker and H. Nawrocki, "Performance Of Graphitized Carbon Cathode Blocks", *Light Metals* 2003, 641-645.
 9. P. R. Tehrani, "Inter-Relating Aluminium Smelting Carbon Cathodes Formulations To Cell Operations And Wear Mechanism", Ph.D thesis, University of Auckland, (2002), 205 pages.
 10. H. Øye, V. de Nora, J.J. Duruz, and G. Johnston, "Properties Of A Colloidal Alumina-Bonded TiB₂ Coating On Cathode Carbon Materials", *Light Metals* 1997, 279-286.
 11. C.E. Ransley, "Producing Or Refining Aluminium, US patent", 3,028,324, 1962.
 12. J.T. Keniry, "The Economics Of Inert Anodes And Wettable Cathodes For Aluminum Reduction Cells", *JOM*, May 2001, 43-47.
 13. Part II of this paper (to be published).
 14. P. Reny and S. Wilkening, "Graphite Cathode Wear Study at Alouette", *Light Metals* 2000, 399-404.